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A Department of Energy Environmental Cleanup Program

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Environmental Restoration Project Standard Operating Procedure

for

# Field Analytical Measurements of Groundwater



NATIONAL LABORATORY

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# **Field Analytical Measurements of Groundwater Samples**

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# Field Analytical Measurments of Groundwater Samples

### 1.0 PURPOSE

This Standard Operating Procedure (SOP) describes procedures for measuring field water quality parameters of groundwater samples at the Los Alamos National Laboratory (Laboratory) Environmental Restoration (ER) Project. Measurement procedures include those for temperature, specific conductance, alkalinity, pH, dissolved oxygen, and turbidity that closely represent water quality conditions in the aquifers.

# 2.0 SCOPE

This SOP is a mandatory document and shall be implemented by all ER Project participants when performing field parameter measurements of groundwater samples for the ER Project.

**Note:** Subcontractors performing work under the ER Project's quality program may follow this SOP for measuring field water quality parameters of groundwater samples. Subcontractor's own procedures may be used provided that the substitute procedures meet the requirements prescribed by the ER Project Quality Management Plan, and have been approved by the ER Project's Quality Program Project Leader (QPPL) before starting the activities.

# 3.0 TRAINING

- 3.1 ER Project personnel using this SOP are self-trained by reading the procedure, and the training is documented in accordance with QP-2.2.
- 3.2 The Field Team Leader (FTL) shall monitor the proper implementation of this procedure and ensure that relevant team members have completed all applicable training assignments in accordance with QP-2.2.

# 4.0 DEFINITIONS

- 4.1 <u>Alkalinity</u> Various soluble mineral salts are found in natural water and arid soils. In water analysis, alkalinity indicates the presence of dissolved constituents that include carbonates, bicarbonates, and/or hydroxides, and occasionally borates, chlorates, silicates, or phosphates, which have the capacity to neutralize acids.
- 4.2 <u>Dissolved oxygen</u> The amount of oxygen dissolved in water, in parts per million (ppm) by weight or in milligrams per liter (mg/L).

- 4.3 <u>Hydrogen-ion activity (pH)</u> The negative log base 10 of the activity of dissociated hydrogen ions [H+]. A measure of the acidity or basicity of a solution, numerically equal to 7 for neutral solutions, increasing with alkalinity and decreasing as acidity increases.
- 4.4 <u>Site-Specific Health and Safety Plan (SSHASP)</u>—A health and safety plan that is specific to a site or ER Project-related field activity that has been approved by an ER Project health and safety representative. This document contains information specific to the project including scope of work, relevant history, descriptions of hazards by activity associated with the project site(s), and techniques for exposure mitigation (e.g., personal protective equipment [PPE]) and hazard mitigation.
- 4.5 <u>Specific conductance</u> (electrical conductivity)— A measure of the ease with which an applied electric field can flow through a material. It is dependant upon the presence of ions (total and relative concentrations, valence, and mobility) and temperature. It is the reciprocal of resistivity and is measured in either siemens (S) or micro-mhos per centimeter (μmho/cm) at 25°C.
- 4.6 <u>Turbidity (nephelometric)</u> Refers to inorganic soilids and organic matter suspended in water. Turbidity is measured in nephelometric turbidity units (NTU) as the intensity of light scattered by the sample particulates relative to a standard reference solution. A turbidity value of 5 NTU or below is the set by the US Environmental Protection Agency (EPA) (EPA, 1986) for sample acceptance criteria for non-filtered samples.

# 5.0 BACKGROUND AND PRECAUTIONS

- 5.1 This SOP shall be used in conjunction with an approved SSHASP. Also, consult the SSHASP for information on and use of all PPE.
- 5.2 Field water quality parameters are normally measured at the time of well-purging and groundwater-sampling activities. Because the value of these parameters begins to change with prolonged exposure to atmospheric conditions, wellhead measurements generally yield the most accurate representation of in situ values. Measurements of temperature, turbidity, specific conductance, and pH made prior to sampling for laboratory analysis are also used as the final indication that a well is purged of stagnant water. Ground water alkalinity and dissolved oxygen are highly dependent on the availability and partial pressures of carbon dioxide and oxygen in the subsurface environment. Preservation of samples selected for turbidity analyses is not practical.

- 5.3 This SOP is to be used in conjunction with ER-SOP-6.01, Purging of Wells for Representative Sampling of Groundwater, and ER-SOP-6.04, Sampling Commercial, Municipal, Domestic, and Monitoring/Characterization Wells.
- 5.4 All waste generated from well development must be handled in accordance with ER-SOP-1.06, Management of Environmental Restoration Project Wastes.

# 6.0 RESPONSIBLE PERSONNEL

The following personnel are responsible for activities identified in this SOP.

- 6.1 ER Project Personnel
- 6.2 Quality Program Project Leader
- 6.3 Team Leader

### 7.0 EQUIPMENT

A checklist of suggested equipment and supplies used to implement this procedure provided in Attachment A. Descriptions of commonly used equipment items and their capabilities are listed below.

- 7.1 <u>Hach 2100 Portable Turbidimeter</u> A collected water sample contained in a vial is inserted into the instrument to optically measure and digitally display turbidity with a measurement range of 0 to 1000 NTU.
- 7.2 <u>Horriba U-10 Water Quality Checker</u>— The instrument sensor is inserted into a sample container of collected water to directly measure six parameters: pH, temperature, dissolved oxygen, electrical conductivity, turbidity, and salinity.
- 7.3 <u>Hach 16900 Digital Titrator</u> A collected water sample contained in a volumetric container is titrated to measure alkalinity with a measurement range of 10 to 4000 mg/L.

# 8.0 PROCEDURE

Note: ER Project personnel may produce paper copies of this procedure printed from the controlled-document electronic file located at website <a href="http://erinternal.lanl.gov/home\_links/Library\_proc.htm">http://erinternal.lanl.gov/home\_links/Library\_proc.htm</a>. However, it is their responsibility to ensure that they are properly trained and are utilizing the current version of this procedure. The author may be contacted if text is unclear. Contact the Document Control Coordinator if the author cannot be located.

**Note:** Deviations from SOPs are made in accordance with QP-4.2, Standard Operating Procedure Development. Procedure deviations are documented in

accordance with QP-5.7, Notebook Documentation for Environmental Restoration Technical Activities.

**Note:** For quality control, field measurements should be repeated, from the beginning, on the same samples that are selected for lab replicates. Follow instructions in the site-specific Sampling and Analysis Plan (SAP) for types and numbers of samples to be taken for quality control.

# 8.1 Pre-operation Activities

- 8.1.1 Assemble the equipment, manufacturer's operator's manuals, and supplies listed in Attachment A.
- 8.1.2 Verify that the equipment and meters are in good working order. The meters should not be dirty or have crusted material on the probes, and the batteries should be charged.
- 8.2 Use of Meters to Measure Field Parameters

This section contains general instructions on the use of meters that measure water temperature, conductivity, pH, alkalinity, dissolved-oxygen, and turbidity. Because there are several types of meters, refer to the operator's manual for specific instructions on the particular instrument being used.

# 8.2.1 Temperature

- 8.2.1.1 Calibrate an immersion thermometer or thermocouple by comparing its readings with those of the reference thermometer at two different temperatures that bracket the temperature range normally measured in the field. Calibration must be done at least annually and whe never the instrument is suspected of having been misused, damaged, or producing erratic or erroneous readings. The instrument should be within ±1.0°C compared with a thermometer calibrated to the National Institute of Standards and Technology standards.
- 8.2.1.2 Obtain a representative groundwater sample as specified in ER-SOP-6.01 and ER-SOP-6.04.
- 8.2.1.3 Place the temperature probe into the groundwater sample, read the temperature upon stabilization, and record the value in the field notebook and/or Water Quality Stabilization Record (see Section 8.3).
- 8.2.1.4 Some pH and electrical conductivity meters are equipped with a temperature probe, which can be used to simultaneously measure sample temperature.

- 8.2.2 Specific Conductance (electrical conductivity)
  - 8.2.2.1 Use a battery operated electrical conductivity meter that is equipped with a temperature compensator and reads directly in μmho/cm at 25°C.
  - 8.2.2.2 Use certified calibration standards to calibrate the conductivity meter. Commercially available standards come in 100, 500, 1,000, 10,000, 50,000, and 100,000 μmho/cm solutions. Use two standard solutions that are within an order of magnitude of the expected sample value.
  - 8.2.2.3 Turn on the meter and adjust the conductivity range selector to the appropriate setting. Rinse the conductivity probe with deionized water and then measure the conductivity of the standard solution.
  - 8.2.2.4 If the meter auto-calibrates, read and record (see Sect 8.3) the conductivity value immediately upon stabilization. If the meter requires manual calibration, digitally enter the appropriate solution value. Remeasure the solution in measure mode and record the value.
  - 8.2.2.5 Obtain a representative groundwater sample as specified in ER-SOP-6.01 and ER-SOP-6.04.
  - 8.2.2.6 Rinse the probe with deionized water. With the meter in measure mode, immerse the probe in the groundwater sample and record the reading (see Section 8.3).
- 8.2.3 Hydrogen-Ion Activity (pH)
  - 8.2.3.1 Refer to the operations manual for calibration instructions specific to the pH meter in use. A general calibration procedure is given below.
  - 8.2.3.2 Commerically prepared buffered calibration solutions are available for pH values of 4.01, 7.0, and 10.01 standard units. At least two standard solutions are required. Check the expiration dates on the buffer solutions to verify that the solutions are still valid for equipment calibration.
  - 8.2.3.3 Choose two buffer solutions that bracket the expected sample pH. Attempt auto-calibration mode by immersing the pH electrode in the first solution and pressing the calibrate button. After the reading has stabilized, record the value (see Section 8.3). Rinse electrode with deionized water and repeat using the second solution. If

- manual calibration is required, digitally enter the appropriate pH values after reading each buffer solution. With the meter in measure mode, remeasure and record the values for each solution.
- 8.2.3.4 Obtain a representative groundwater sample as specified in ER-SOP-6.01 and ER-SOP-6.04.
- 8.2.3.5 With the meter in measure mode, rinse the electrode with deionized water and place it into the groundwater sample. Wait for the pH to stabilize and then record the reading (see Section 8.3).

# 8.2.4 Dissolved Oxygen

- 8.2.4.1 Most dissolved-oxygen meters may be auto-calibrated on site by simply exposing the probe to saturated air and pressing the calibration button.
- 8.2.4.2 Obtain a representative groundwater sample as specified in ER-SOP-6.01 and ER-SOP-6.04.
- 8.2.4.3 Place the dissolved-oxygen probe into the groundwater sample and record the final value of dissolved-oxygen concentration to the nearest 0.1 mg/l (see Section 8.3).

# 8.2.5 Turbidity

- 8.2.5.1 Use Hach Model 2100 or 2100A or an acceptable equivalent that is capable of turbidity measurements (nephelometric) in conformance with EPA's Method 180.1 (EPA, 1983).
- 8.2.5.2 Most turbidimeters are precalibrated and need a zero adjustment before being used for testing. To zero a turbidimeter, place a vial with a standard solution of 0 NTU into the sample chamber and press the zero button. The solution can be either purchased or produced with deionized water and a filter system.
- 8.2.5.3 Obtain a representative groundwater sample as specified in ER-SOP-6.01 and ER-SOP-6.04.
- 8.2.5.4 Fill a vial with the recommended amount of groundwater sample. To get accurate results, the vial must be clean and free of defects. Discard any vials with scratches. Wipe the vial clean with lint-free tissues before inserting it into the chamber (it is important to keep the vials clean). To

avoid smudges, handle each vial by its top rim only. Record turbidity readings (see Section 8.3).

# 8.2.6 Alkalinity

- 8.2.6.1 Refer to the operations manual for titration instructions specific to the digital titrator in use. A general calibration procedure is given below.
- 8.2.6.2 Select the appropriate sample volume and titration cartridge corresponding to the expected range of alkalinity concentration in the sample. This will be at most 100 mLs or a dilution of the sample to 100 mLs.
- 8.2.6.3 Add one Phenolphthalein indicator power pillow to the sample. If the solution turns pink, titrate till colorless, by adding incremental amounts of sulfuric acid. Record the number of digits required and follow the equation in the operators manual. You must swirl the sample while adding the acid and keep adding acid until color is consistent. Proceed to next step if color does not change to pink.
- 8.2.6.4 Add one Bromcresol Green-Methyl Red indicator power pillow to the sample. Titrate till you reach the endpoint indicated by the operators manual, by adding incremental amounts of sulfuric acid. Record the number of digits required and follow the equation in the operators manual. You must swirl the sample while adding the acid and keep adding acid until color is consistent.

## 8.3 Documentation

Document all information as indicated in ER-SOP-1.04. Information should be recorded in either field notebooks or Daily Activity Log forms (Attachment E in ER-SOP-1.04) and on the Water Quality Sampling Record (Attachment B in ER-SOP-6.01) and also, if needed, on the Water Quality Stabilization Record (Attachment B—form and completion instructions). Information that should be recorded includes

- equipment model and serial number,
- expiration date of calibration solution.
- lot number of calibration solution,
- manufacturer of calibration solution,
- date and time of calibration,
- calibration measurements.

- water sample field parameter measurements, and
- date and time of each set of measurements.

# 8.4 Postoperation Activities

- 8.4.1 When the sampling is completed, or at the end of the field day, carefully clean the outside of the sampling instruments with a damp disposable towel to remove any visible dirt. Clean and decontaminate the equipment as specified ER-SOP-1.08 and replenish supplies.
- 8.4.2 Return the equipment to the equipment manager. Report any malfunctions, performance deviations, or damage.
- 8.4.3 Restore the site to the presampling conditions as described in the site-specific documents.

#### 8.5 Perform Lessons Learned

During the performance of work, **ER Project personnel** shall identify, document and submit lessons learned, as appropriate in accordance with QP-3.2, Lessons Learned, located at <a href="http://erinternal.lanl.gov/home\_links/Library\_proc.htm">http://erinternal.lanl.gov/home\_links/Library\_proc.htm</a>.

# 9.0 REFERENCES

ER Project personnel using this procedure should become familiar with the contents of the following documents to properly implement this SOP.

- ER Project Quality Management Plan, located at <a href="http://erinternal.lanl.gov/home\_links/Library\_proc.htm">http://erinternal.lanl.gov/home\_links/Library\_proc.htm</a>.
- QP-2.2, Personnel Orientation and Training
- QP-3.2, Lessons Learned
- QP-4.2, Standard Operating Procedure Development
- QP-4.3, Records Management
- QP-4.4, Record Transmittal to the Records Processing Facility
- QP-5.7, Notebook Documentation for Environmental Restoration Technical activities.
- ER-SOP-1.04, Sample Control and Field Documentation
- ER-SOP-1.06, Management of Environmental Restoration Project Wastes
- ER-SOP-1.08, Field Decontamination of Drilling and Sampling Equipment
- ER-SOP-6.01, Purging of Well for Representative Sampling of Groundwater

- ER-SOP-6.04, Sampling Commercial, Municipal, Domestic, and Monitoring Wells
- EPA, "Methods for Chemical Analysis of Water and Wastes," EPA-600-4-79-020, Environmental Monitoring and Support Laboratory, (Office of Research and Development, Cincinnati, Ohio, March 1983).
- EPA, "RCRA Groundwater Monitoring Technical Enforcement Guidance Document," (OSWER, U.S. Government Printing Office, Washington, D.C., 1986).

# 10.0 RECORDS

The **FTL** is responsible for submitting the following records (processed in accordance with QP-4.4, Record Transmittal to the Records Processing Facility) to the Records Processing Facility:

- 10.1 Water Quality Sampling Record form (Attachment B in ER-SOP-6.01)
- 10.2 Water Quality Stabilization Record form (Attachment B)
- 10.3 Daily Activity Log form (Attachment E in ER-SOP-1.04) and field notebook

# 11.0 ATTACHMENTS

Attachment A: Equipment and Supplies Checklist for Field Analytical Measurements of Groundwater Samples (1 page) located at <a href="http://erinternal.lanl.gov/Quality/user/forms.asp">http://erinternal.lanl.gov/Quality/user/forms.asp</a>.

Attachment B: Water Quality Stabilization Record (form and completion instructions) (2 pages) located at <a href="http://erinternal.lanl.gov/Quality/user/forms.asp">http://erinternal.lanl.gov/Quality/user/forms.asp</a>.

Using a token card, click here to record "self-study" training to this procedure.

If you do not possess a token card or encounter problems, contact the RRES-ECR training specialist.

# **Equipment and Supplies Checklist for Field Analytical Measurements of Groundwater Samples** For Temperature (one of the following) Calibrated, partial-immersion thermometer graduated in 0.5°C within the range of 0-50°C and the manufacturer's operating manual Or A thermocouple calibrated within ±0.5°C greater than the range 0-50°C or expected use and the manufacturer's operating manual Or The built-in thermometer in the pH or conductivity meter For Specific Conductance Specific-conductance meter and the manufacturer's operating manual Calibration solutions For pH pH meter and manufacturer's operating manual le in Section 11.0. Standard pH solutions For Dissolved Oxygen Oxygen meter with sensor and manufacturer's operating manual For Turbidity Turbidity meter with a range of 0-400 NTU and manufacturer's operating manual For Alkalinity Alkalinity titrator kit and the manufacturers operating manual Forms Water Quality Sampling Record Water Quality Stabilization Record Daily Activity Log forms or field notebook Other Any additional supplies listed in associated procedures, as needed Any PPE listed or required in the SSHASP Los Alamos ER-SOP-6.02 **Environmental Restoration Project**

Water Quality Stabilization Record										
Date			ocus Area	Shee			d of			
Site Wor	k Plan									
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				Param	neter ivie	asurements				
Time	Total Volume Withdrawn		рН	EC (μmho/cm)	Temp (°C)	Dissolved Oxygen	Turbidity (NTU)	Comments		
	(gal.)	(Bore Volume)		(μππο/οπ)	( )	(mg/l)	(1110)			
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Alkal	inity (ı	mg/L of CaC	O <sub>3</sub> )							
ER-SOP-6.02					Los Alamos Environmental Restoration Project					

# **Water Quality Stabilization Record Completion**

# **Header Information:**

- Date—Date of sampling.
- 2. Sheet Number—Number all the sheets that are used for this activity, by day or by some practical unit.
- 3. Technical Area (TA)—Two-digit number which indicates the TA in which the activity is being performed.
- 4. Focus Area—Focus Area in which the activity is being performed.
- 5. Site Work Plan—Title of plan.
- 6. Field Team Member Identification—Print your name and position title, then sign.
- 7. Monitor Well/Characterization ID

#### Time:

The time when a field measurement of purged water was performed in the format HH:MM.

# Total Volume Withdrawn:

Using a bucket or flow meter, the field team member will note the number of gallons of water purged from the well at the time that a field measurement is taken. This entry is cumulative and represents the total volume of water purged before sampling may begin.

A second column is provided so that the field team member can equate gallons to bore volumes purged (see equation on page 1 of the Water Quality Sampling Record—Attachment B in ERP-SOP-6.01).

Parameter Measurements (Record each time a field measurement of purged water is performed.):

- 1. Negative log 10 of Hydrogen-Ion Activity—The pH units of the sample.
- 2. Specific Conductance—The specific conductance of the water in micro-ohms per centimeter in ( $\mu$ ohm/cm) at 25°C.
- 3. Temperature—The temperature of the water in degrees Celsius (°C).
- 4. Dissolved Oxygen—The dissolved oxygen content of the water in milligrams per liter (mg/l).
- 5. Turbidity—The turbidity of the water in nephelometric turbidity units (NTU).
- 6. Alkalinity The alkalinity of the water in mg/L CaCO<sub>3</sub>

Comments: Note any other pertinent information.